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Department of Chemical Engineering

B.Tech Thesis on

Study on the thermal Pyrolysis of Medical Waste (Plastic syringe) for the Production of useful Liquid Fuels

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CERTIFICATE

This is to certify that the work in this thesis entitled "**Thermal pyrolysis of Plastic medical waste (plastic syringes) for the Production of useful Liquid Fuels**" submitted by Abhishek Dash (108CH037) in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2008-2012 in the department of Chemical Engineering, National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the thesis is his bona fide work.

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(Abhishek Dash)

108CH037

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NOMENCLATURE

MTOE	Million tons of oil equivalents
TERI	The Energy and Resources Institute
GoI	Government of India
GDP	Gross Domestic Product
MNRE	Ministry of New and Renewable Energy
TGA	Thermo-gravimetric Analysis
PID	Proportional-integral-derivative
ASTM	American Society for Testing and Materials
FTIR	Fourier Transform Infrared Spectroscopy
GCV	Gross Calorific Value

ABSTRACT

Energy crisis have led to a vast research on various alternative sources of energy in order to cope up with the growth in standard of living of all human beings across the world. And Waste disposal poses a problem which is increasingly difficult to ignore. While the increasing volumes of generated waste are a problem, the types of waste being generated further complicate the challenge of disposal. Waste-to energy is an obvious replacement for medical waste incinerators whose numbers are likely to decline due to more stringent emission standards. The high plastic content of medical waste is looked at as a potential feedstock for a novel pyrolytic reactor. Hence, various technologies and processes are evolved to utilize the waste resource efficiently. Pyrolysis is one of the latest technologies which have the potential to provide valuable liquid and gaseous fuels from these medical waste sources. In this work, thermal pyrolysis of plastic medical waste (plastic syringes) will be performed in a semi batch reactor at a temperature of 450°C for the production of pyrolytic oil. The physical properties analysis of liquid product is in comparable range with physical properties of commercial transportation fuels.

INTRODUCTION

1. Introduction

Nowadays, Energy has become a stature symbol for economic growth and human development. It has been observed that energy consumption shows a two way trending with economic development, one is growth which relies on availability of cost effective and environmental friendly energy sources whereas on the other hand, level of economic development which is observed to be reliant on energy demand.

In a growing economy like India, and China energy is an essential building block of development. In the past decades, India's energy consumption has been increasing at one of the fastest rates in the world due to rapid population growth and economic development, with its primary commercial energy demand increasing by 6% from 1981 to 2001 as reported by Planning Commission, Government of India [1]. India accounted for 3.5% of the world. Commercial energy demand in the year 2003 making it fifth highest consumer in the world in terms of primary energy consumption [2]. However, per capita energy consumption in India is still very low compared to other developing/developed countries irrespective of its overall increase in energy demand.

Indian energy sector has witnessed rapid growth and revolutionary developments in areas like resource exploration and exploitation, energy sector reforms and capacity additions in order to meet its demands on its course to become a developed country. Still, India is lagging behind to meet the increasing energy demands because of rapid urbanization, multiplying population and progressing economy even after the efforts made in energy supply growth and resource augmentation. These energy shortages are affecting tremendously to Indian economy as it has to rely heavily on imports.

1.1. Trends in Energy Resources

India has been gifted well enough with both exhaustible and renewable energy resources. Coal, Oil, and Natural Gas are the three primary commercial energy sources on which India has relied upon from decades. Till the end of 1980s, India's energy policy was mainly based on availability of native resources which made coal the largest source of energy. India lacks in oil assets and therefore has to depend on crude imports to meet a major share, around 70% of its needs in 2009 [3]. However, India's primary energy mix has changed a lot over the decades but coal has remained the most significant & ample fossil fuel in India till now and is expected to be the dominant source for energy till 2030 with a contribution of around 51% of India's energy need [4]. Currently, coal contributes around 52% (283 MTOE) of commercial energy requirements whereas petroleum products accounts for 30-35%, nearly 9 per cent by natural gas and 2% by nuclear and 2% hydro energy [4].

Indian economy relies heavily on commercial fuels but a sizeable quantum of energy requirements, especially in the rural household sector, is met by non-commercial and traditional energy sources such as fuel wood, crop residue, liquid mass and animal waste, human and draught animal power. The usage of such sources of energy is estimated at around 155 MTOE/annum [5]. However, higher quality and more efficient commercial energy source shave started to replace the traditional energy resources.

In Planning Commission 2002, it was desired by Government of India to achieve 10% GDP (Gross Domestic Product) growth rate during Eleventh Five Year Plan and to maintain an average growth rate of about 8% for the next 15 years. It confirmed that country's requirements for energy and supporting infrastructure is going to increase rapidly and in order to facilitate the policy makes to make prompt decisions, estimation of the total energy requirements as well as

look at the economic, environmental, and geopolitical implications of India's alternative energy pathways for the next few decades is very crucial. Demographic profile, change in lifestyle, and consumer preferences determined the level of useful energy demands, whereas the availability, prices of resources and technologies influenced the levels and patterns of final energy requirements in the future[6].

In order to estimate the total energy requirements in future, The Energy and Resources Institute (TERI, Office of the Principle Scientific Adviser, GoI) modeled a system to determine the total commercial energy requirements over the period of 2001-2031 under different scenarios such as BAU (business as usual), REN (aggressive renewable energy), NUC (high nuclear capacity), EFF (high efficiency), HYB (hybrid), LG (low growth), HG (high growth) and HHYB (high hybrid) which almost dictated the routes toward future and increase in energy consumption as the cost for the route. The findings are shown in table 1:

Table 1: Variation in Total Energy Consumption in MTOE (Million Tons of Oil Equivalent)[6]

Scenario	2001/02	2006/07	2011/12	2016/17	2021/22	2026/27	2031/32
BAU	285	391	527	749	1046	1497	2123
REN	285	391	524	740	1033	1479	2097
NUC	285	391	527	749	1030	1455	2061
EFF	285	379	479	623	838	1131	1542
HYB	285	379	478	619	823	1101	1503
LG	285	361	456	605	816	1134	1579
HG	285	435	638	962	1438	2186	3351
HHYB	285	405	544	760	1087	1576	2320

As reported by TERI, the total commercial energy consumption in BAU scenario is estimated to increase up to 2123 MTOEs, i.e. by 7.5 times, till 2031. A comparative study between effects of different economic growth scenario such as LG (economy grows at 6.7% with

a GDP of 5.9%) and HG (economy grows at 10% with GDP 8.6%) on energy requirements showed that commercial energy requirement will increase to only about 1579 MTOE by 2031 in LG scenario, whereas the energy requirements can be as high as 3351 MTOE in the HG scenario. The REN and NUC scenario analysis also cleared it that the plans of enhancing the exploitation of hydro energy, nuclear energy and renewable energy sources will not help much when compared to total commercial energy requirements by 2031. It was estimated that the contribution of hydro, nuclear, and renewable energy forms together will increase by about 6 times over the period 2001-31, but they can contribute only 4.5% of the total commercial energy requirements. Thus, the dependence on the three conventional energy forms: coal, oil, and gas will continue to remain high for the next few decades. Increase in efficiency in power, industrial and transport sectors, on both demand and supply side, showed a significant scope of reducing overall energy consumption. In the HYB scenario, energy requirements by the year 2031 would be of the order of those in the LG scenario, while those in the HHYB scenario will be in the range of requirements in the BAU scenario.

A fuel wise commercial energy consumption analysis was also made to check the dependence on various fuels. It was seen from figure 1 that Natural Gas will be a preferred option for power generation and fertilizer production but coal and oil will remain dominant fuels till next few decades. However, the HYB scenario indicates some potential to reduce coal and oil requirements as compared to the BAU scenario only with adequate, timely policy and technological intervention.

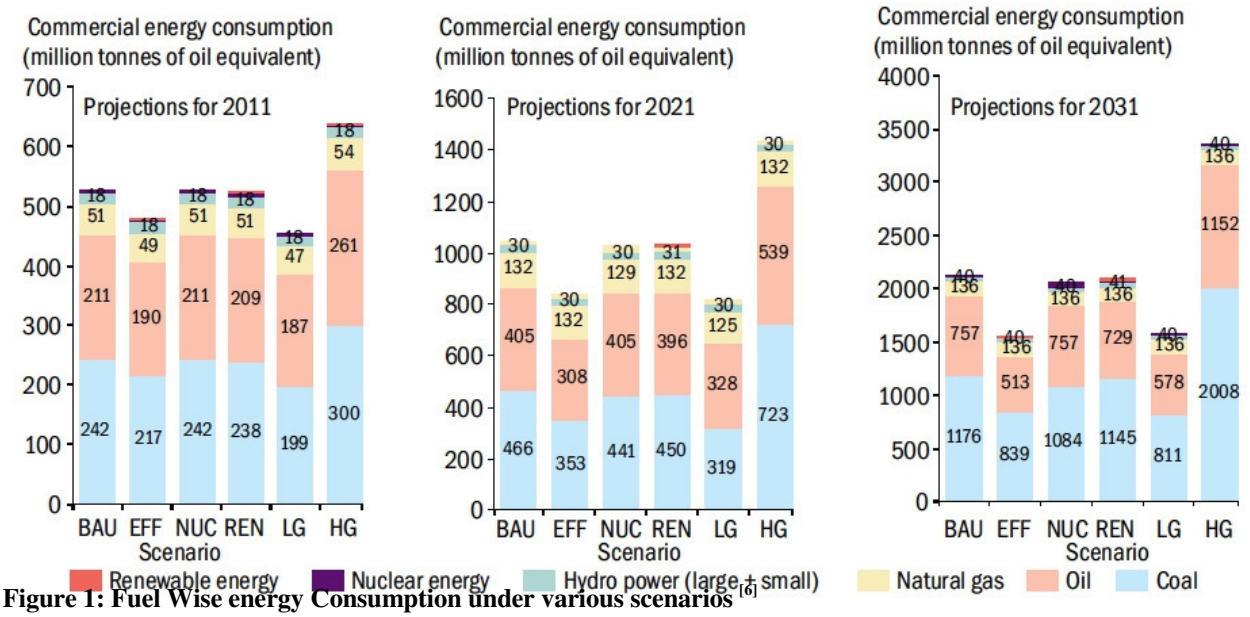

Figure 1: Fuel Wise energy Consumption under various scenarios [6]

The report have clearly shown that in order to reduce dependence on imports of conventional energy fuels and to withstand energy security viewpoint, the country have to undertake every possible options on the demand and supply side simultaneously so as not only to reduce its total energy requirements but also diversify its fuel resource mix. An integrated energy planning exercise with the following key elements were suggested:

- more thrust to exploration and production of coal, involvement of private sector.
- Energy security in hydrocarbons, engage private sector to produce hydrocarbons.
- Reduce coal requirements and consumption of petroleum products, Natural gas to be the preferred fuel.
- Renewable energy resources to be made competitive, and targeted to spread it in remote areas and for decentralized power generation.
- Enhanced efforts to tap alternative indigenous energy sources.
- Reduce transmission and distribution loss.

1.2. Potential of Waste Plastics

Used Low density polyethylene from household and industries are recognized to be a major environmental problem. There are several methods for disposal of municipal and industrial LDPE wastes, i.e. landfill, incineration, true material recycling, and chemical recovery. Landfill treatment and incineration destruction are quite expensive and may raise problems with unacceptable emissions. True material recycling, i.e. to convert the waste material into products that can be reused, can significantly reduce the net cost of disposal. However, it is generally accepted that true material recovery is not a long-term solution to treat waste LDPE.

Chemical recycling were investigated, through which waste plastics were converted into fuel oil and valuable chemicals.

Thermal and catalytic degradation of waste plastics are two kinds of chemical recycling processes. The main drawbacks of thermal degradation are wide product distribution and requirement of high temperatures, typically more than 500 °C and even up to 900 °C. Since thermal degradation demands relatively high temperatures and its products require further processing for their quality to be upgraded, catalytic degradation of polymer waste offers considerable advantages. Catalytic pyrolysis gives a means to solve these problems.

Suitable catalysts have the ability to control both the product yield and product distribution from polymer degradation as well as to reduce significantly the reaction temperature. LDPE was both decomposed thermally and catalytic in a continuous reactor via as an oxidative media in the temperature range of 400–500 °C. [7]

So for the studies reported in the literatures about waste LDPE pyrolysis have been carried out in the presence of various expensive catalysts and derived oils of high boiling point range at comparatively high temperature.[7]

1.3. Plastic Waste Management

Due to population increase, the demand for plastic products has steadily increased over the last 40 years. Since plastics are non-liquid degradable, they cannot be easily returned to the natural carbon cycle; hence the life cycle of plastic materials ends at waste disposal facilities. There are several methods for disposal of municipal and industrial plastic waste as shown in figure 2, i.e. landfill, incineration (energy recovery), true material recycling (similar recycled product or monomer recovery), and chemical recovery. The suitable treatment of plastic wastes is one of the key questions of the waste management and is important from energetic, environmental, economical and political aspects [18]. In most developed societies domestic organic waste, including plastics packaging, is disposed of in sanitary land filled or by incineration. During early 2000, the largest amount of plastic wastes is disposed of by land filling (65-70%), and incineration (20-25%). Recycling is only about 10%.

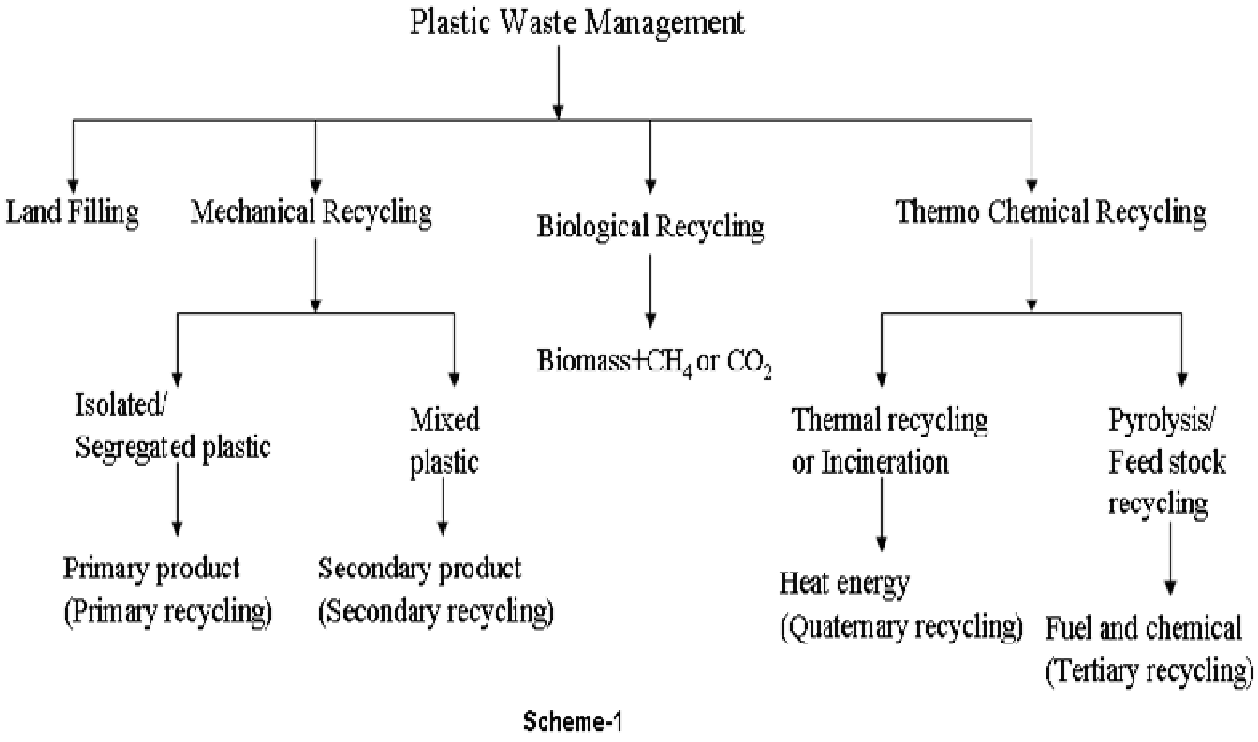

Figure 2. Types of plastic waste management

Scheme-1

Land filling (shortage of land, rising cost of land, increased legislation)

Mechanical recycling (High energy process, low quality of secondary product)

Liquid logical recycling (applicable for liquid degradable plastics)

Chemical recycling by Pyrolysis (Produce fuel & monomer). Use of waste plastics, cheap and reusable catalyst, no emission, thus a green method of waste management.

1.4. Pyrolysis

Pyrolysis is a thermo-chemical process for conversion of plastic waste by heating the feedstock at high temperature in absence of air which produces gaseous products which is then condensed to give liquid fuels consisting of pyrolytic oil or liquid-oil. Almost 70-80% of gaseous products are converted into liquid fuels providing a good quantity of liquid fuel which then can be enhanced. The reason for popularity of this process is that it derives a good quantity of liquid fuel, from feedstock, which has properties very close to commercial transportation fuels and hence can be upgraded or modified to replace transportation fuel. Moreover, it also provides some amount of gaseous and solid products which have higher market value as they can also be used as a source of energy.

1.5. Literature Review

Pyrolysis of low-density polyethylene (predominantly in Plastic Syringes) was studied in order to relieve environmental pollution and recover the monomer or fuel. First, efficiency of oil production was studied according to the variation of reaction conditions such as reaction temperature, types of additives and contacting method. In non-catalytic LDPE pyrolysis, isothermal reaction was almost similar to non-isothermal reaction. Light oil was produced with low reaction temperature (430 degree Celsius) in the isothermal reaction, but low heating rate caused light oil production in the non-isothermal reaction [Park et al, 2002].

Recycling of waste plastics is thus an important issue, and it has been researched worldwide. As a result, the technical recycling method has been widely diversified in the present [Fouhy et al., 1993; Kim, 1996]. Three kinds of recycling methods for waste plastic have been proposed. First energy is recovered from the waste plastics by conversion into fi2el oils. Second, waste plastic is recycled by material recycling or mechanical process. This method, however, may not be a long-tern1 solution to the present problem [Willimns, 1993; Song and Hyun 1999].

The third method is called chemical recycling. Waste plastics are converted into the corresponding monomer or advanced chemical, which then is re-synthesized. Among these three methods, chemical recycling is the most economically sound. Converted fuels or chemicals could be merged into standard petrochemical or petroleum refining industry operation [Shelleyet al., 1992; Ide, 1984]. In fact DuPont has developed techniques to decompose waste PET into ethylene glycol and dimethyl terephthalate, which can be used for the reproduction of pure PET resin [Hirose, 1998]. Among the six main plastics, low density polyethylene (LDPE) is used in various fields such as in plastic grocery bags, water hoses, garbage cans, film, containers, etc. LDPE is also known as a very difficult plastic to pyrolyze, but the amount of waste LDPE generation is increasing with its use. In this study, pyrolysis of low density polyethylene (LDPE) was studied [Songip, 1993]. LDPE was thermally decomposed to recover oil. First, efficiency of oil production was analyzed according to the variation of reaction conditions such as reaction temperature, types of additives, types of the catalysts, and the contacting method of sample and the catalysts. Second, oil composition was analyzed and compared for each reaction condition.

Effect of temperature was studied without catalyst. Isothermal pyrolysis was observed in the range of 440-500 degree Celsius and non-isothermal reaction was studied from 0 to 440 degree Celsius with 7 degree elevation (table 2). For non-isothermal reaction, retention time increases in the low temperature region, but the ratio of low molecular weight oil increased and the product oil showed brighter colour. As reaction temperature increased, reaction time was shortened and the ratio of low molecular weight oil decreased. At 440 degree Celsius the highest product yield (84.0 wt%) and low molecular weight hydrocarbon (<C11, 24.4wt%) was achieved with retention time of 132 min. For isothermal reaction, ratio of low molecular weight compound within the product oil increased as temperature is lowered.

Table 2. Effect of the reaction temperature on the pyrolysis

Reaction temperature (°C)	Reaction time (min)	Yield (wt%)	$\leq C_{11}$ (wt%[a])	Yield of $\leq C_{11}$ (wt%)
440	132	84.0	29.0	24.4
450	90	83.0	26.0	21.6
460	95	86.7	20.0	17.3
470	61	90.5	21.0	19.0
500	40	94.3	15.0	14.2
0-440 (7°C/min)	166	76.0	31.0	23.6

[a]Carbon analysis by using ASTM, D-2887; $\leq C_{11}$, yield (wt%) of the carbon number below 11.

MATERIALS

&

METHODS

2. Materials and Methods

2.1. Raw Material

The Medical waste (Waste plastic syringes) has been collected from CWS hospital, Rourkela and only the body of the syringe was used discarding the needle., before use so as to minimize voids inside the reactor as well as to fill maximum amount of Plastic waste syringe into the reactor.

2.2. Thermo-Gravimetric Analysis

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the plastic syringe has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample plastic syringe was done with DTG60 instrument. Around 20-30 milligrams of sample shredded plastic was taken and heated up to a temperature of 800°C and a residence time of 1 minute at 800°C was allowed. TGA was performed both in air and nitrogen atmospheres at a heating rate of 25°C/Min and one observation was taken at a heating rate of 20°C/Min in air medium. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of shredded plastic syringe takes place.

2.3. Experimental Procedure

It consisted of a reactor-furnace system in which the furnace temperature was maintained constant using a PID controller. At the outlet of reactor, a condenser was attached to condense the vapors coming out of it. The condensed liquid was collected in a collecting jar at the end of condenser. The plastic shreds is filled in a reactor of 300 ml and the reactor is kept in the furnace for heating at constant temperature, temperature at which maximum yield of liquid product is obtained. When the reaction starts, vapors coming out of reactor through the provided outlet are

condensed in a condenser as shown in figure 3. Water is circulated as cooling medium in the condenser via a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected contains oily water and liquid-oil. Oily water is basically water with some dissolved hydrocarbons. Oily-water and liquid-oil is further separated by difference in their density.

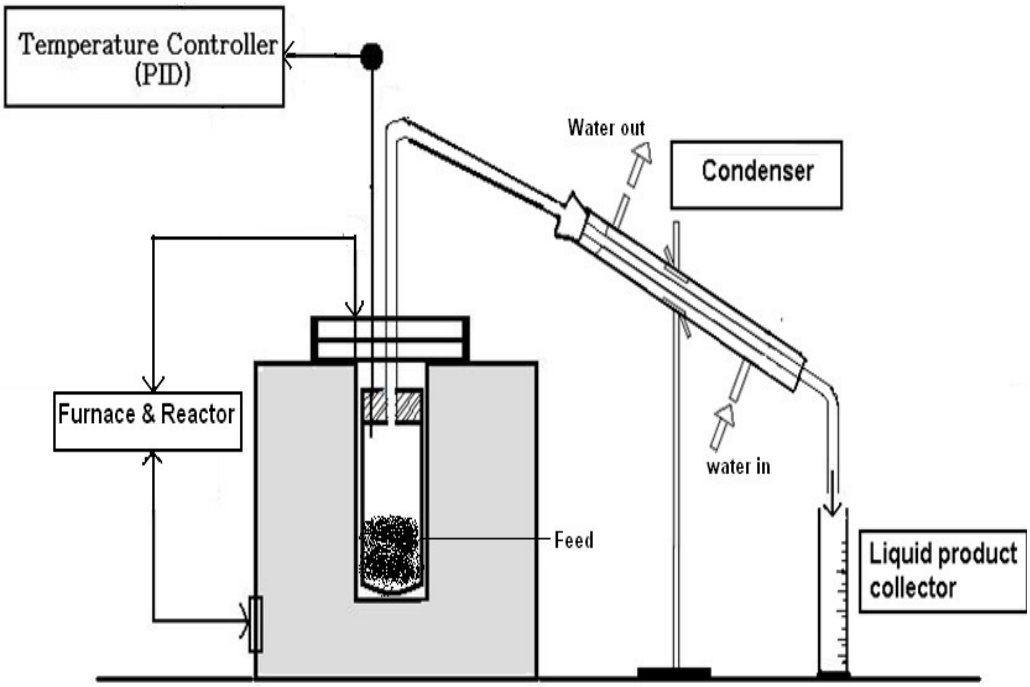

Figure 3 : Experimental Set-Up

2.4. Sample Pyrolysis Runs

Once the temperature range was found out then sample pyrolysis runs were done with 30gms of plastic shreds in that range at intervals of 50°C to determine the temperature at which max. yield of liquid product is obtained. During sample runs various data like reaction time, yield of char, and yield of liquid product were noted down. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is plotted. Variation in reaction time with temperature was also plotted.

2.5. Characterization of Raw Material

The shredded syringe plastics were analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

2.5.1 Proximate Analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using *ASTM D3172 - 07a* [19] method.

2.5.2. Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage. And sum of these components is subtracted from 100, it gives oxygen percentage composition.

2.5.3. Calorific Value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for plastic syringe using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

2.6. Physical Characterization of Liquid-Oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the liquid-oil was determined using the following standard methods shown in table 3.

Table 3: Standard Methods for Physical Property Analysis

Physical Property	Method
Density	ASTM D1298 - 99
Kinematic Viscosity	ASTM D445 - 11
Conradson Carbon	ASTM D189 - 06(2010)e1
Flash Point	ASTM D6450 - 05(2010)
Fire Point	ASTM D1310 - 01(2007)
Pour Point	ASTM D5853 - 09
Calorific Value	ASTM D5468 - 02(2007)
Distillation Boiling Range	ASTM D2887 - 08
Cetane Index	ASTM D4737 - 10

2.7. Chemical Characterization of Liquid-Oil

2.7.1. FTIR

In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer.

2.7.2. GC-MS

Gas Chromatography - Mass Spectrometry of the pyrolytic oil was performed using a GC-MS-OP 2010[SHIMADZU] analyzer in Sargam Laboratory, Chennai to determine the chemical compounds present in the oil. The following GC-MS conditions have been used for determining the chemical compounds in the liquid product:

GC Conditions:

Column Oven Temperature: 70˚C

Injector Temperature : 240˚C

Injection Mode : Split

Split Ratio : 10

Flow Control Mode : Linear Velocity

Column Flow : 1.51 ml/min

Carrier Gas : Helium 99.9995% purity

Injection volume : 1 microliter

Column Oven Temperature Program:

Rate	Temperature(˚C)	Hold Time(min)
-	70.0	3.0
10	300	9 [35.0 mts total]

Column:VF-5ms

Length : 30.0m

Diameter: 0.25mm

Film Thickness: 0.25um

MS condition:

Ion source temp: 200 °C

Interface temp: 240°C

Scan range: 40 – 1000 m/z

Solvent cut time: 5mins

MS start time: 5(min)

MS end time : 35 (min)

Ionization: EI (-70ev)

Scan speed: 2000

RESULTS

&

DISCUSSION

3. Results & Discussion

3.1. TGA analysis of waste plastic syringe

Pyrolysis is heating of a substance in absence of air at a particular temperature. The TGA curve (Figure 4) curve showed that the maximum thermal degradation of the raw material takes place in the temperature range of 270–500 °C in all observations. The point where the derivative of wt% becomes zero gives the range of degradation.

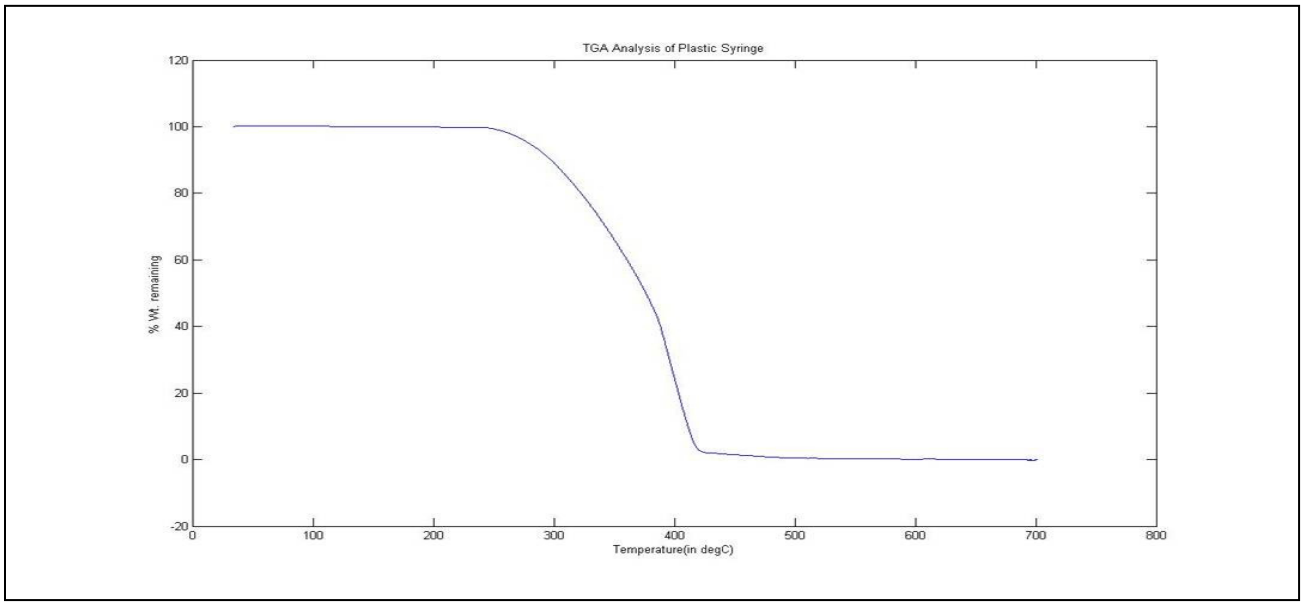

Figure 4: TGA analysis curve of sample (plastic syringe)

3.2. Sample Pyrolysis Runs

The plot (Figure 5) between yield of liquid, solid and gaseous products vs. temperature clearly shows that the yield of liquid product increases with increases in temperature in the range of 400-450 °C and then it starts decreasing. Thus maximum yield of liquid product is 83 wt% at the temperature 450 °C which indicates it as effective pyrolysis temperature for medical plastic syringes. Reaction time decreases with increase in temperature. The product distribution by thermal pyrolysis of waste plastic syringe is shown in table 4.

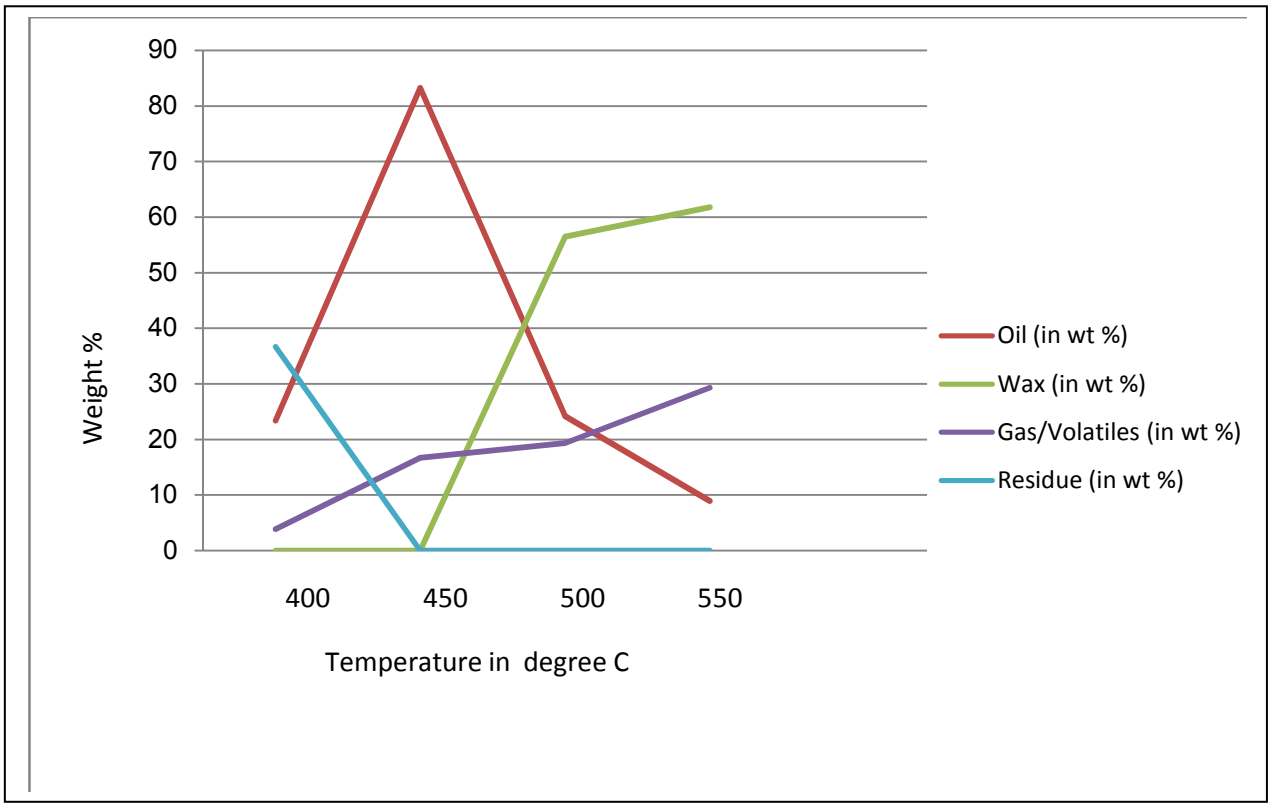

Figure 5: Graph showing liquid, wax, residue and gas content at different temperatures

Temperature (in deg celcius)	Oil (in wt %)	Wax (in wt %)	Gas/Volatiles (in wt %)	Residue (in wt %)	Reaction Time (in mins)
400	23.4	0	3.834	36.7	245
450	83.3	0	16.7	0	100
500	24.2	56.5	19.3	0	65
550	8.92	61.8	29.28	0	44

Table 4: Product distribution by thermal pyrolysis of waste plastic syringe

3.5. Chemical Composition of Liquid product

3.5.1. FTIR Analysis

FTIR analysis suggests that the functional groups like alcohols, ketones, carboxylic acids, esters, alkanes, alkenes, alkynes, amide, nitriles, nitro compounds, ethers, aromatic rings may be present in the liquid-oil. It has to be confirmed with gas chromatography results.

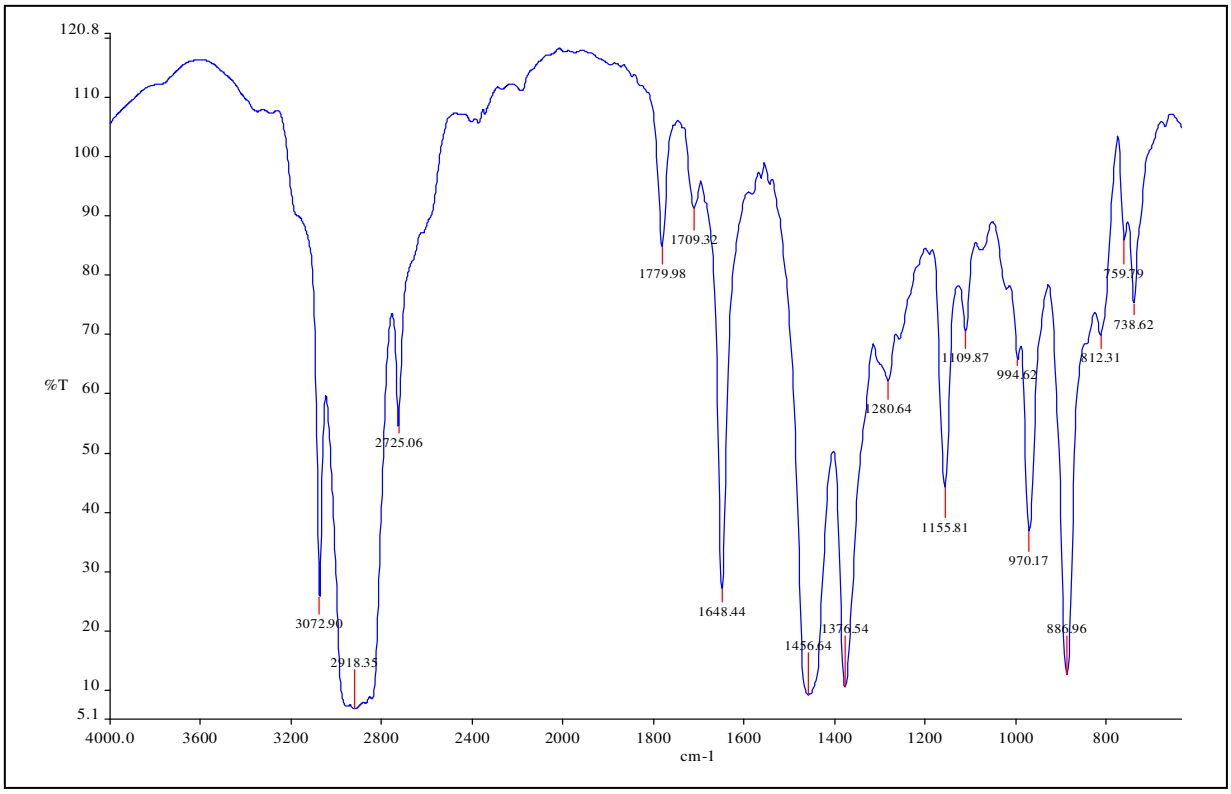

Figure 6: FTIR Graph

Table 5: FTIR Compound and Frequency Table

Compound Type	Frequency
Alkanes	2850-2960
Alkenes	1640-1680
C-H Aromatic rings	3000-3100
Aldehydes, Ketones, Carboxylic Acids, Esters	1670-1760
Nitro compounds	1260-1390
Amines	1020-1340
Alkenes	675-1100
Alkynes	610-750

3.5.2. Gas Chromatography-Mass Spectrometry

The chemical composition of the liquid product was determined using GC-mass spectrometry. The compounds present in the liquid-oil were identified by comparing the chromatogram obtained with standard chromatogram data available. It was found that liquid product consisted of around 56 compounds as shown in table 6.

Table 6: Chemical Composition of Liquid-Oil

Compound	Formula	Area%
heptane, 3,3,6-trimethyl-	$C_{10}H_{22}$	1.3
heptane, 2,5,5-trimethyl-	$C_{10}H_{22}$	1.32
3-octadecene, (e)-	$C_{18}H_{36}$	6.63
(3e)-3-octadecene	$C_{18}H_{36}$	4.9
1-tridecanol	$C_{13}H_{28}O$	1.12
heptafluorobutyric acid, n-pentadecyl ester	$C_{19}H_{31}F_7O_2$	0.65
(2,4,6-trimethylcyclohexyl) methanol	$C_{10}H_{20}O$	2.39
cyclohexane, 2,4-diethyl-1-methyl-	$C_{11}H_{22}$	0.83
2,4-diethyl-1-methylcyclohexane	$C_{11}H_{22}$	0.51
cyclohexane, 2,4-diethyl-1-methyl	$C_{11}H_{22}$	0.48
tetradecane, 4-methyl-	$C_{15}H_{32}$	0.55
4,6-dimethyldodecane	$C_{15}H_{32}$	0.34
2-hexadecen-1-ol, 3,7,11,15-tetramethyl-, [r-[r*,r*-(e)]]- (t-phytol)		0.54
1-nonadecene	$C_{19}H_{38}$	9.34
1-nonadecene	$C_{19}H_{38}$	5.71
1-pentadecene	$C_{15}H_{30}$	7.97
heneicosyl heptafluorobutyrate	$C_{25}H_{43}F_7O_2$	1.19
Cyclododecanemethanol	$C_{13}H_{26}O$	2.95
Cyclododecylmethanol	$C_{13}H_{26}O$	0.84
7,11-dimethyl-10-dodecen-1-ol	$C_{14}H_{28}O$	0.54
nonadecyl pentafluoropropionate	$C_{22}H_{39}F^5O_2$	3.99
hexadecylsulfonyl chloride	$C_{16}H_{33}ClO_2S$	2.06
hexadecylsulfonyl chloride	$C_{16}H_{33}ClO_2S$	1.11
sulfonyl chloride, 1-hexadecane	$C_{16}H_{33}ClO_2S$	2.81
tetracosyl heptafluorobutyrate	$C_{28}H_{49}F_7O_2$	1.35
Cyclododecanemethanol	$C_{13}H_{26}O$	0.69

Compound	Formula	Area%
(2,2,6,6-tetramethylcyclohexyl)methanol	$C_{11}H_{22}O$	3.36
10-dodecen-1-ol, 7,11-dimethyl-	$C_{14}H_{28}O$	0.45
isotridecanol-	$C_{13}H_{28}O$	0.96
cyclohexane, 1-ethyl-2-propyl-	$C_{11}H_{22}$	0.23
cyclooctan, 1-methyl-3-propyl-	$C_{12}H_{24}$	0.51
nonadecyl pentafluoropropionate	$C_{22}H_{39}F_5O_2$	0.29
tetratriacontyl heptafluorobutyrate	$C_{38}H_{69}F_7O_2$	3.97
tetratriacontyl heptafluorobutyrate	$C_{38}H_{69}F_7O_2$	1.06
eicosyl heptafluorobutyrate	$C_{24}H_{41}F_7O_2$	4.32
hexacosyl heptafluorobutyrate	$C_{30}H_{53}F_7O_2$	0.98
hexacosyl pentafluoropropionate	$C_{29}H_{53}F_5O_2$	0.46
eicosyl heptafluorobutyrate	$C_{24}H_{41}F_7O_2$	0.61
tetratriacontyl heptafluorobutyrate	$C_{38}H_{69}F_7O_2$	1.78
2,4,6-trimethyl-11-dodecen-1-ol	$C_{15}H_{30}O$	3.08
cyclooctane, 1-methyl-3-propyl-	$C_{12}H_{24}$	0.67
1-ethyl-2-propylcyclohexane	$C_{11}H_{22}$	0.48
octatriacontyl trifluoroacetate	$C_{40}H_{77}F_3O_2$	1.89
hexatriacontyl pentafluoropropionate	$C_{38}H_{69}F_7O_2$	1.14
cyclohexan, 1,2,3,5-tetraisopropyl-	$C_{18}H_{36}$	2.82
1,2,3,5-tetraisopropylcyclohexane	$C_{18}H_{36}$	0.55
tetratriacontyl pentafluoropropionate	$C_{22}H_{39}F_5O_2$	1.21
hexacosyl heptafluorobutyrate	$C_{30}H_{53}F_7O_2$	0.86
1,2,3,5-tetraisopropylcyclohexane	$C_{18}H_{36}$	2.56
tetratriacontyl heptafluorobutyrate	$C_{22}H_{39}F_5O_2$	0.54
1,2,3,5-tetraisopropylcyclohexane	$C_{18}H_{36}$	1.8
cyclohexane, 1,2,3,5-tetraisopropyl-	$C_{18}H_{36}$	0.19
hexacosyl heptafluorobutyrate	$C_{30}H_{53}F_7O_2$	0.54
tetratriacontyl heptafluorobutyrate	$C_{22}H_{39}F_5O_2$	0.21
octatriacontyl trifluoroacetate	$C_{40}H_{77}F_3O_2$	0.39

3.5. Physical properties analysis of obtained liquid product

Table7: for physical properties

Tests	Results Obtained	Test method
Specific Gravity @ 15°C/15°C	0.8288	IS:1448 P:16
Density @ 15°C in kg/cc	0.8281	IS:1448 P:16
Kinematic Viscosity @ 40°C in Cst	2.97	IS:1448 P:25
Kinematic Viscosity @ 100°C in Cst	1.14	IS:1448 P:25
Viscosity Index	NA	----------
Conradson Carbon Residue	0.05%	IS:1448 P:122
Flash Point by Abel Method	Minus 6 ^{o}C	IS:1448 P:20
Fire Point	Minus 2 ^{o}C	IS:1448 P:20
Cloud Point	3 ^{o}C	IS:1448 P:10
Pour Point	18 ^{o}C	IS:1448 P:10
Gross Calorific Value in Kcal/Kg	10,179 Kcal/kg	IS:1448 P:6
Sulphur Content	Less than 50 ppm	IS:1448 P:33
Calculated Cetane Index (CCI)	48	IS:1448 P:9

From comparison of physical properties of liquid fuel with transportation fuels [Table 8] it can be observed that plastic syringe liquid fuel is lighter than water and has very low viscosity which is suitable for injection of fuel in the engine even at lower temperatures. Flash point of liquid fuel is in comparable range and hence will ensure safe storage. Calorific value is in the similar range of that of gasoline and diesel which is actually good enough for we have a fuel which will have somewhat comparable performance of engine. As it can be observed from Table 8, the properties of liquid fuel were in similar range to that of other commercial oils.

Table 8: Comparison of fuel properties

Properties / Fuels	Specific Gravity 15°C/15°C	Kinematic Viscosity @40°C(cst)	Flash Point	Pour Point	GCV (MJ/Kg)	Chemical Formula
Plastic Syringe Oil	0.8288	2.97	-6	18	44.8	C_8-C_{40}
Gasoline[20]	0.72-0.78	-	-43	-40	42-46	C_4-C_{12}
Diesel[21]	0.82-0.85	2-5.5	53-80	-40 to -1	42-45	C_8-C_{25}
Bio-Diesel[21]	0.88	4-6	100-170	-3 to 19	37-40	C_{12}-C_{22}
Heavy Fuel Oil[22]	0.94-0.98	>200	90-180	-	40	-

INDUSTRIAL

SCALE-UP

&

ECONOMIC

ASSESSMENT

4. Industrial Scale-Up and Economic Assessment

4.1. Aim

Design an industrial unit of capacity 12 tons/day for producing liquid fuel by thermal pyrolysis of Plastic syringe.

4.2. Raw Material

Shredded plastic syringe

4.3. Products

Product	Use
Plastic syringe Pyrolytic Oil	Used as Liquid-fuel.
Fuel Gas	Non-condensable vapors having high calorific value.

4.4. Process

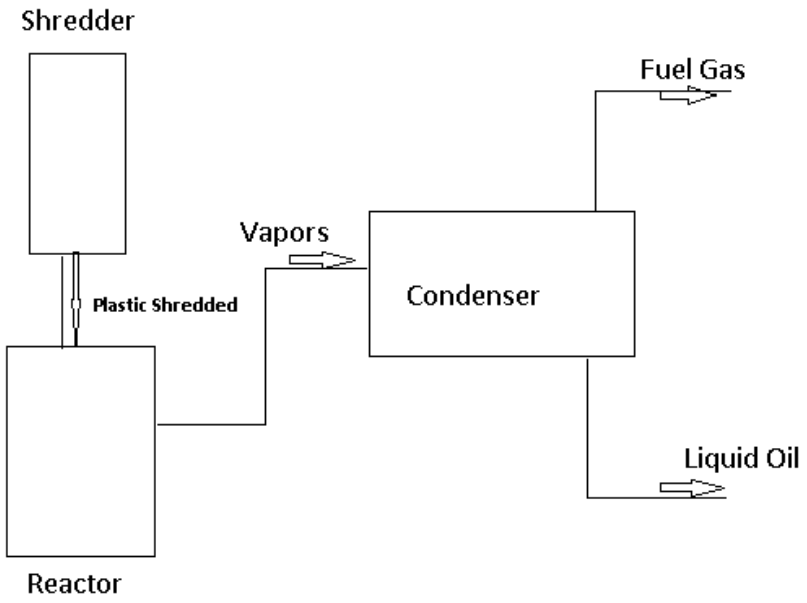

Figure 7: Process flow diagram of Pyrolysis unit

4.5. Material Balance

1 kg plastic syringe (shredded) produces ➡ 0.3125 Kg Non-Condensable Vapors (Fuel Gas)

➡ 0.6875 Kg Liquid-Fuel

Let us design the unit to process 12 tons of plastic syringe (shredded) in a single run.

12 tons of plastic syringe (shredded) products ➡ 8250 Kg of Liquid-fuel

➡ 3750 Kg Fuel Gas

4.6. Energy Balance

4.6.1. Energy Balance for Reactor

Due to the complex nature of pyrolysis processes of plastic medical waste involving lots of simultaneous reactions, it is very difficult to keep an account of all processes while doing energy balance. Thus, for the sake of convenience, we measured the overall energy required for the pyrolysis of different amount of plastic syringe (shredded) by connecting an energy meter across the furnace. A linear relationship was found out from the plot of Mass vs. Energy consumed.

Table 9: Energy-Mass Analysis

Mass (gm)	Q (KJ)
30	2449
40	2480
50	2511
60	2542

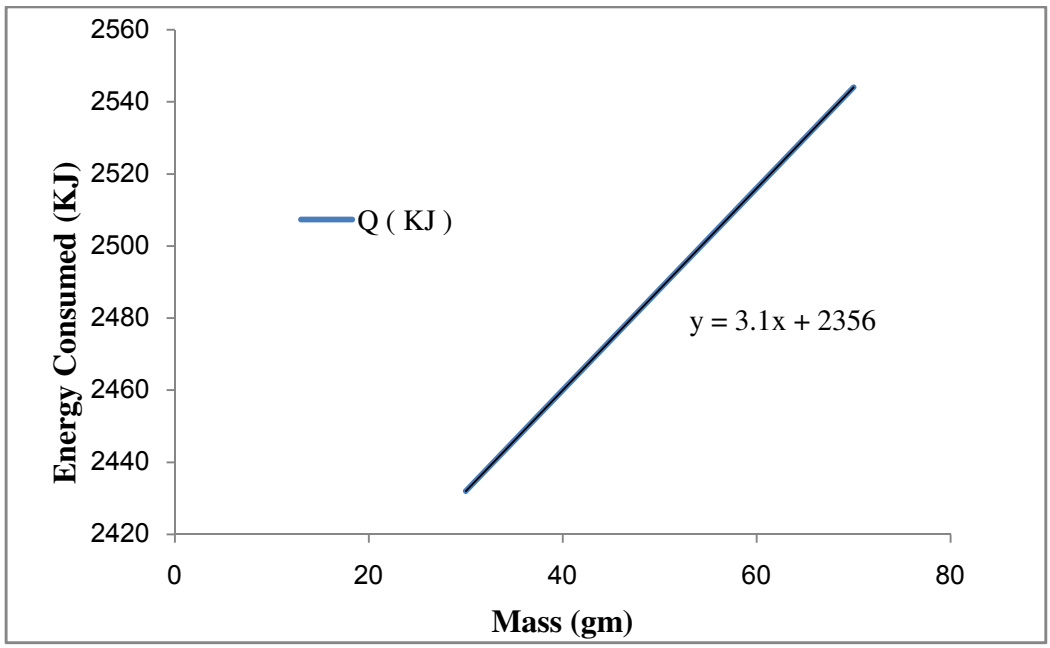

Figure 8: Mass-Energy consumption

Now using the linear relation, a rough estimation of energy required for pyrolysis of 12tons of plastic syringe (shredded) was found out to be 37,200MJ. This energy is the amount of overall energy consumed by the process, i.e. energy to raise temperature of plastic syringe (shredded) from 35°C to 475°C along with energy consumed for pyrolysis reaction, whereas in industry the case will be different. Although the process is a semi-batch process but the furnace won't be allowed to cool down to room temperature after every run as it will cost a lot of energy loss. So, energy consumed is expected to be less than 37,200 MJ. Since it is a rough estimation, so calculation are done with 37,200 MJ only.

4.6.2. Energy balance for Condenser

As the operating temperature of the reactor and furnace system is 475°C so we assume temperature of the vapors coming out of the reactor to be at around 420°C.

Now, *(Vapors from Reactor) = (Fuel Gas) + (Liquid-Fuel))*

So, input for condenser = 12000 Kg of vapors which comprises of 3750 Kg of Non-condensable (Fuel Gas) and 8250 kg of condensable liquid product. Here also a very rough estimation has to

be done in order to determine energy recovered while condensing. Here, the process is condensation of mixture of hydrocarbon vapors. In order to evaluate the energy recovered during condensation and design the condenser mole fraction of each component of hydrocarbon vapor mixture is required with their specific heat capacity, thermal conductivity, viscosity, heat of vaporization, etc. which are not available. So, in this estimation, the hydrocarbon vapor mixture is considered as a single component hydrocarbon vapor with specific heat of vapor as 0.5 KJ/Kg K since it varies in the range of 0.5-3 KJ/Kg K for hydrocarbon vapors at constant pressure.

Specific heat of liquids can be obtained using Kopp's rule from its chemical composition, i.e. C, H, N, S and O composition. As the data is not furnished due to unavailability of equipment so average values for C, H, N, S and O composition is taken from the literature as the properties of our liquid-fuel lies considerably in the range of other similar products. Thus,

C = 86.78; H = 12.61; N = 0.5; S = 0.072; O = 0.038

From Koop's rule, Specific Heat = 1.75 KJ/Kg K.

Now, distillation range for liquid-oil is,

Table 10: Distillation range for Liquid-Oil

Initial Boiling point	70°C
Final Boiling Point	384°C

Now,

(Total Energy Recovered)= (Energy by Fuel Gas)+(Energy by Liquid fuel)

Energy by fuel gas = 3750*0.5*(475-40) = 8,15,625 KJ = 815.6 MJ

Energy by liquid-fuel = 8250*0.5*(475-384) + 8250*1.75*(384-70)

= 4908750 KJ = 4908.7 MJ

Total Energy Recovered = (815.6 + 4908.7) = 5724.35 MJ

Amount of cooling water @30°C required = 5724350/(4.186*40) = 4749.2 Kg = 34.18 tons

4.7. Equipment Size

4.7.1. Reactor

Cylindrical shape reactor made of carbon steel operating at 14.7 psi.

The reactor is assumed to work in a similar way to coke ovens used for coking of coal with a capacity of 12 tons processed at single run with a residence time of 20 hours.

Total Energy required for one run = 37,200 MJ = 35.25 M Btu

Time between two consecutive runs for discharging and loading = 1 hour

Total time for one run = 21 hours

Total no of runs per year = (365*24)/21 = 417 runs

Energy required per hour, Q = (35.25)/20 = 1.76 M Btu/hr

4.7.2. Condenser

1-4 Shell and tube exchanger with 21.25 inch shell inner diameter with a baffle spacing of 5 inch and 158 no of 16 inch long 13 BWG tubes with an outer diameter of 1 inch and a square pitch of 1.25 inch. Combined dirt factor of 0.003 should be provided.

Flow rate of vapors = (12000 Kg)/21 = 571.428 Kg/hr

Flow rate of cooling water = 65000/21 = 3095.23 Kg/hr

Inlet temperature of vapors = 475°C

Outlet temperature of vapors = 70°C

Inlet temperature of cooling water = 30°C

Outlet temperature of cooling water = 70°C

LMTD = 157.67°C R = 405/40 = 10.125S = 40/(475-30) = 0.0898 F_T = 0.9

Δt = 0.9*157.67 = 141.94°C

Shell Side (Cooling water):

Flow area = (21.25*0.25*5)/ (144*1.25) = 0.1475 ft^2 = 137.03 cm^2 = 0.014 m^2

Mass Velocity = (3095.23)/ (0.014) =2, 21,087 Kg/hrm^2 =61.4132 Kg/m^2s

Equivalent diameter = 0.99/12 = 0.0825 ft = 0.025 m

Viscosity of water = 0.547*10^{-3} N s/m^2

Thermal conductivity of water = 0.6 W/m K

Reynolds number = (0.025*61.4132)/ (0.547*10^{-3}) = 2806.82

j_H = 28

h_o = 28*(0.6/0.025)*((4186*0.547*10^{-3})/0.6)$^{(1/3)}$ = 1050.14 W/m^2 K

Tube Side (Hot fluid):

Flow area = (158*0.515)/ (144*4) = 0.141 ft^2 = 0.0131 m^2

Mass velocity = 571.428/ (0.0131) = 43620.52 Kg/hrm^2 = 12.11 Kg/m^2 s

Viscosity of hydrocarbon vapor @240°C = 1.9*10^{-5} Kg/m s

Thermal conductivity of hydrocarbon vapor = 0.1385 W/m K

Reynolds number = (0.021*12.11)/ (1.9*10^{-5}) = 13384.73

L/D = 16/0.0675 = 237

j_H = 40

h_i = 40*(0.1385/0.021)*((475*1.9*10^{-5})/(0.1385))$^{(1/3)}$ = 106.168 W/m^2 K

h_{io} = 106.168*0.81 = 85.996 W/m^2 K

Clean overall coefficient, U_C = (85.996*1050.14)/(85.996+1050.14) = 79.486 W/m^2 K

Overall design coefficient:

Total Surface Area = 158*16*0.2618 = 662 ft^2 = 61.5 m^2

U_D= (5724.35*10^6)/((21*3600)*(61.5*130.57)) = 9.42 W/m^2 K

Dirt Factor = (U_C - U_D)/(U_C*U_D) = (79.48-9.42)/(79.48*9.42) = 0.094 m^2K/W

4.8. Cost Analysis

Cost analysis provides a rough estimate of the total investment required to setup a plant of particular capacity, operating cost of the plant and production cost of the product. Cost analysis data will enable us to determine whether setting up such a plant is economically feasible and beneficial to society or not.

Total investment consists of two parts:

• Fixed Capital: - Total cost of plant ready for start-up.

• Working Capital: - Additional investment needed, over and above the fixed capital, to start the plant and operate it to the point when income is earned.

4.8.1. Factorial Method to Determine Total Investment:

$C_f = f_l * C_e$

Where, C_f = Fixed Capital Cost

f_l = Lang Factor depending on type of process

Ce = Total delivered cost of all major equipment.

• Prepare material & energy balance, preliminary flow sheets, size major equipment and select material of construction.

• Estimate purchase cost of major equipment using literatures.

• Calculate Fixed Capital using Table 10.

• Working Capital = 10-20% of Fixed Capital.

		Process Type		
Sl. No.	**Item**	**Fluids**	**Fluids-Solids**	**Solids**
1	Major Equipment Purchase Cost (PCE)	1	1	1
f1	Equipment Erection	0.4	0.45	0.5
f2	Piping	0.7	0.45	0.2
f3	Instrumentation	0.2	0.15	0.1
f4	Electrical	0.1	0.1	0.1
f5	Buildings, Process	0.15	0.1	0.05
f6	Utilities	0.5	0.45	0.25
f7	Storage	0.15	0.2	0.25
f8	Site Development	0.05	0.05	0.05
f9	Ancillary Buildings	0.15	0.2	0.3
	Total Physical Plant Cost (PPC) = PCE*	3.4	3.15	2.8
	Total Physical Plant Cost (PPC)	1	1	1
f10	Design & Engineering	0.3	0.25	0.2
f11	Contractor's Fee	0.05	0.05	0.05
f12	Contingency	0.1	0.1	0.1
	Fixed Capital = PPC*	1.45	1.4	1.35

Table 11: Lang factors for estimation of fixed capital costs

4.8.1.1. Major Equipment Costs

Shredder

A CE certified shredder for plastics like PP, PS, PVC with capacity of 150-2000kg/hr is used for this purpose

Cost of shredder @2012 = $12,800

Reactor

Cost of cylindrical reactor made of carbon steel operating at 14.7 psi with an energy intake capacity (15 m^3) of 1.592MBtu/hr = $44,312 (2004 basis, PCI = 444).

Cost of reactor @2012 (PCI = 665) = (665/444)*45718 = $66,368

Condenser

A 1-4 fixed head shell and tube heat exchanger made of stainless steel with heating surface area of 61.5 m^2 and operating at pressure range of 10 psi is required.

Cost of exchanger @2004 = $52,000; Cost of exchanger @2012 = $77,882

Storage Tanks

Cost of Storage Tank 1 of capacity 50 m^3 for storing liquid-fuel (floating roof) @2004 = $37,404

Cost of Storage Tank 1 @2012 = $56,022

Thus major equipment purchase cost = shredder + reactor + condenser + 3 storage tanks

= $ 210072 = Rs 10,503,600

4.8.1.2. Total Investment

Major Equipment Purchase Cost (PCE) = Rs 9,082,700

Total Physical Plant Cost (PPC) = 1.95*PCE= Rs 17,711,265

Fixed Cost = 1.35*PPC = Rs 23,910,207

Working Capital = 0.10*Fixed Cost = Rs 2,391,020

Total Investment = Fixed Capital + Working Capital = Rs 26,301,228

4.8.2. Operating Cost

It is the cost of producing the product and is needed to judge viability of project and to choose between alternate processes.

Annual Production Cost = A + B + C (From Table 7) (12)

Production Cost (per Kg) = $\frac{Annual\ Production\ Cost}{Annual\ Production\ Rate}$ (13)

Table 12: Operating costs

Sl. No.	Item	Typical Values
	Variable Costs	
1	Raw Materials	From Material Balance
2	Miscellaneous Materials	10% of item (5)
3	Utilities	From Flow Sheet
4	Shipping & Packaging	Usually Negligible
	Sub Total A =	1+2+3+4
	Fixed Costs	
5	Maintenance	5-10% of Fixed Capital
6	Operating Labors	From Manning Estimates
7	Laboratory Costs	20-23% of item (6)
8	Supervision	20% of item (6)
9	Plant Overheads	50% of item (6)
10	Capital Charges	10% of Fixed Capital
11	Insurance	1% of Fixed Capital
12	Local Taxes	2% of Fixed Capital
13	Royalties	1% of Fixed Capital
	Sub Total B =	5+6+7+8+9+10+11+12+13
	Direct Production Costs =	A+B

Raw Material

Cost of Raw material = 417*10*12000 = 50040000

Miscellaneous Materials

Cost of Miscellaneous Materials = 0.10*0.05*23,910,207= Rs 119,551

Utilities

Chilled Water @30°C = ((417*65*1)/100)*(665/444) = $406 = Rs 20,298

Electricity = {1.5*{(417*37,200) – (7952.2*417)}}/100

= $182944 = Rs 91, 47,250

Cost of Utilities = Rs 91, 67,548

Maintenance

Cost of Maintenance = 0.05*23,910,207 = Rs 1,195,510

Operating Labors

Cost of Operating Labor = 20*3*500*365 = Rs 1,09,50,000

Laboratory Costs

Laboratory Costs = 0.2*1,09,50,000 = Rs 21,90,000

Supervision

Supervision Cost = 0.2*1,09,50,000 = Rs 21,90,000

Plant Overheads

Plant Overheads = 0.5*1,09,50,000 = Rs 54,75,000

Capital Charges

Capital Charges = 0.1*23,910,207 = Rs 2,391,020

Insurance

Insurance = 0.01*23,910,207 = Rs 2, 39,102

Local Taxes

Local Taxes = 0.02*23,910,207 = Rs 4,78,204

Royalties

Royalties = 0.01*23,910,207 = Rs 2, 39,102

Direct Production Costs = Rs 121479865

Sales Expense + General Overheads + R & D = 0.2*121479865 = Rs 24295973

Annual Production Cost = Rs 121479865 + 24295973 = Rs 145775838

Income from sales of Liquid-Fuel = 417*8250*50 = Rs 189213750

Income from sales of Fuel Gas = 417*3750*4.4767*1.32 = Rs 9240580

Total Income from Sales = Rs 198454330

Net Profit = Rs 52678492.

CONCLUSION

6. Conclusion

Waste plastic is a grey area of concern and pyrolysis though a difficult process can be made feasible with better optimization and equipments (catalytic cracking instead of thermal). The plastic syringe used is a mixture LDPE (Low density polyethylene), PP (Poly Propylene), and some traceable amounts of PS (Poly-Styrene). Maximum yield of liquid product is 83 wt% by thermal pyrolysis of shredded plastic syringes at temperature 450 °C. Plastic syringe/waste has high volatile matter content and high calorific value in the range of diesel oils which is converted to liquid fuel. The liquid fuel obtained shows comparable fuel properties and can be treated as moderate grade commercial fuels. In order to utilize it as commercial transportation fuel certain enhancement in properties like density, viscosity, corrosiveness and volatility have to be taken care off. The liquid-oil contains nearly 56 chemical compounds of varying carbon chain length from C_8-C_{40} and functional groups such as alkanes, alkenes, alkynes, alcohols, ketones, aldehydes, C-H aromatics rings and nitro compounds.

Industrial scale-up and economic assessment was performed for the process and assumptions had to be taken to simplify the calculations. The result of the economic assessment was overwhelmingly satisfactory as it made a profit of 52 Million INR annually.

In order to have proper economic assessment the following things are required to be taken care off: (a) compositional analysis of mixture of hydrocarbon vapors coming out of reactor before getting condensed; (b) properties like specific heat, thermal conductivity, kinematic viscosity, latent heat of vaporization, etc. of every of component present in the hydrocarbon mixture are to be determined; (c) specific heat of liquid-fuel is also required.

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